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(19)



(54) GLASS-CERAMIC ARTICLES AND METHODS OF MAKING THE SAME

(71) We, OWEN-ILLINOIS, INC. a corporation organised and existing under the laws of the State of Ohio, United States of America, of Toledo, State of Ohio, United States of America, (assignee of DANIEL ROBERT STEWART), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of making high strength, generally low thermal expansion glass-ceramic articles from lithium aluminosilicate glass compositions, nucleated with both TiO_2 and ZrO_2 and containing fluorine as a glass constituent and to the articles made thereby.

The present invention provides methods of obtaining high strength generally low thermal expansion glass-ceramic articles from lithium aluminosilicate composition nucleated with both TiO_2 and ZrO_2 and containing fluorine by ion exchanging lithium ion of the articles with e.g. sodium or potassium ion to provide modulus of rupture for the article of at least 85,000 psi to 90,000 psi even after mild abrasion. High strength glass-ceramic articles having an abraded modulus of rupture as high as 100,000 psi or more have been made according to the invention. The use of fluorine as a glass constituent and the ion-exchanging of the lithium ion with a sodium or potassium ion having a synergistic effect on the glass-ceramic articles by greatly increasing the strength as measured by the abraded modulus of rupture.

The low expansion glass-ceramic articles of the present invention generally exhibit the property of breaking with dicing rather than shattering.

Generally, as is well known in the art, articles are formed from the crystallizable glass composition and heat treated to produce glass-ceramic articles.

According to the present invention, there is provided a method of obtaining a glass-ceramic article having a modulus of rupture

of over 85,000 psi after mild abrasion, the method comprising the steps of

(1) applying to a surface of the glass-ceramic article containing lithium ions an ion-exchange medium containing alkali metal ions having a larger ionic radius than the lithium ions the glass-ceramic article comprising in percent by weight:

Ingredients	Percent by weight	
SiO_2	60—75	55
Al_2O_3	15—30	
LiO_2	3—5.5	
F_2	0.2—0.8	60
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	0—2	
$\text{TiO}_2 + \text{ZrO}_2$	2.5—10	

wherein TiO_2 and ZrO_2 are present together and the balance, if any, of said article consists of other compatible ingredients and wherein the molar ratio of $\text{R}_2\text{O} + \text{RO}:\text{Al}_2\text{O}_3$ is 0.95 to 0.5:1, where R_2O is the total alkali metal oxide content and RO is the total divalent metal oxide (as hereinafter defined) content.

(2) maintaining on the surface of the glass-ceramic article the ion exchange medium at an elevated temperature sufficiently high and for a period of time sufficient to exchange the lithium ions in the glass-ceramic article with the alkali metal ions of the ion exchange material to provide a compressive stress layer in the article, and

(3) cooling the article to a temperature at which said ion exchange does not occur to provide a glass-ceramic article having a strength of at least 85,000 psi after mild abrasion. The amount of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is generally less than 2% and the amount of $\text{TiO}_2 + \text{ZrO}_2$ mixture is generally 3 to 8%. When referred to herein, the ratio of $\text{R}_2\text{O}:\text{Al}_2\text{O}_3$ or $\text{R}_2\text{O} + \text{RO}:\text{Al}_2\text{O}_3$ is a molar ratio.

According to the present invention, there is provided a glass-ceramic article comprising a composition in percent by weight.

[Price 25p]

76 P 1577 AP

	Percent		Preferred	
	Ingredients	by weight	Ingredients	
5	SiO ₂	60—75	SiO ₂	61—71
	Al ₂ O ₃	15—30	Al ₂ O ₃	18—28
	Li ₂ O	3—5.5	Li ₂ O	3.5—4.8
	F ₂	0.2—0.8	F ₂	0.3—0.6
	Na ₂ O + K ₂ O	0—2	Na ₂ O + K ₂ O	<1.5
	TiO ₂ + ZrO ₂	2.5—10	TiO ₂ + ZrO ₂	3.2—5.0
			(both present)	
			R ₂ O + RO/Al ₂ O ₃	0.9:1 to 0.6:1
			Optimum	
10			65—71	
			19—27	
			4.5—4.8	70
			0.3—0.55	
			<1.2	
15			3.2—4.8	
			0.8:1 to 0.6:1	75
20	wherein TiO ₂ and ZrO ₂ are present together and the balance, if any, of said article consists of other compatible ingredients and wherein the molar ratio of R ₂ O + RO:Al ₂ O ₃ is 0.95 to 0.5:1 where R ₂ O is the total alkali metal oxide content and RO is the total divalent metal oxide (as hereinafter defined) content, in which the surface layer of said glass-ceramic has a compressive stress provided by ion exchanging lithium ions in the glass-ceramic with alkali metal ions having a larger ionic radius than said lithium ions.			
	As used herein the term R ₂ O is intended to mean any alkali metal oxide e.g. the oxides of lithium, potassium and sodium.			
25	As used herein the term "divalent metal oxide" is intended to mean any alkaline earth metal oxide, (e.g. calcium, magnesium and strontium) zinc oxide or any mixtures thereof.			
30	The amount of TiO ₂ and ZrO ₂ mixture is preferably in the range of 3 to 6% by weight although beneficial results are obtained with amounts as low as 2.5% and as high as 7 or 8 or even up to 10%. For the best results the nucleating agent is a mixture of TiO ₂ and ZrO ₂ the preferred amount of TiO ₂ being 1 to 2% by weight and optimally 1.4 to 1.8%.			
35	The surface of the glass-ceramic article is maintained with the ion exchange material at an elevated temperature sufficient high and generally below the strain point of the glass-ceramic material for a period of time to exchange the lithium ions in the glass-ceramic article with alkali metal ions of the ion exchange material to provide a compressive stress layer in the article and thereafter the article is cooled to a temperature at which the ion exchange does not occur to provide a high strength, generally low thermal expansion glass-ceramic article having a strength of at least 85,000 psi even after mild abrasion. After cooling, the ion exchange medium is removed by washing to provide the outstanding high strength glass-ceramic article.			
40				
45				
50				
55	The glass-ceramic article starting material (containing fluorine as a glass constituent) in the present invention has preferred and optimum ranges of the ingredients in percent by weight as follows:			
	The glass-ceramic starting material containing fluorine can be prepared as described in United States patent No. 3,489,577 which is directed to similar glass-ceramic compositions. However, the fluorine content must be closely controlled and restricted to the limited amounts indicated. This patent is hereby incorporated by reference.			
	In the present invention, the ion exchange medium is preferably a sodium nitrate salt bath or a potassium nitrate salt bath although other methods of applying an ion exchange medium to the surface of the glass-ceramic article can be used. Methods of ion exchanging and ion exchange mediums are disclosed in patents such as the Weber United States patent No. 3,218,220, the Grubb and LaDue United States patent No. 3,498,773, the Denman United States patent No. 3,428,513 and the Graham United States patent No. 3,473,906, which patents are hereby incorporated by reference. It is preferred that the ion exchange temperature be below the strain point of the glass-ceramic material but, as seen in United States patent No. 3,498,773, the temperature can be at or above the strain point for a short time — say 5 to 30 minutes.			
	In accordance with the present invention, the elevated temperature used in the heat treating step conducted on the thermally-crystallizable glass compositions to provide the glass-ceramic article is generally 1800° to 2200° F., the preferred range being 2100° to 2200° F.			
	The ion exchanging step to provide the compressive stress layer on the glass-ceramic article can be conducted, as for instance, seen in the working examples, in a molten alkali salt bath such as sodium nitrate or potassium			

nitrate at 750° F. for 8 hours or at 1000° F. for $\frac{1}{2}$ or 1 hour.

5 The following examples are intended to illustrate the present invention and not to limit it in any way. Examples 1, 11, 12 and 16 are included for comparative purposes only.

EXAMPLES 1—5.

10 A series of ion-exchange, fluorine-containing glass-ceramic samples were made to show the great increase in the modulus of rupture property (even after mild abrasion) by the use of fluorine as a glass constituent and ion exchange of sodium or potassium ions from the ion exchange medium with lithium ions in the glass-ceramic composition. Glass-ceramic articles were prepared from starting glass compositions as well known in the art to provide

the compositions set forth in the table of results (see Table 1). Also in the Table 1, modulus of rupture data is shown including the outstanding results obtained by the use of a sodium nitrate bath and a potassium nitrate bath. The results were obtained on samples which were rods made of glass-ceramic material containing fluorine. The synergistic effect of the fluorine in the P_2O_5 -containing glass-ceramic composition and the ion exchange of lithium for either sodium or potassium can be seen from the results of Table 1.

Also, as seen in Table 1A, compositions 1 and 3 were ion exchanged in a sodium nitrate bath at 1000° F. for $\frac{1}{2}$ hour and for one hour, the modulus of rupture data on composition 3 (containing fluorine) showing an increase of about 110 psi upon ion exchange.

TABLE 1

	Theoretical		Theoretical			
	1	2	1	3	4	5
SiO ₂	61.96	61.36	61.96	63.35	63.1	62.85
Al ₂ O ₃	25.89	25.64	25.89	26.6	26.6	26.6
Li ₂ O	4.62	4.58	4.62	4.75(4.75)	4.75	4.75
TiO ₂	1.83	1.83	1.83	1.4	1.4	1.4
ZrO ₂	2.75	2.75	2.75	2.15	2.15	2.15
Na ₂ O	0.55	0.55	0.55	1.0	1.0	1.0
K ₂ O	0.55	0.55	0.55			
P ₂ O ₅	1.85	1.83	1.85			
F ₂	0	0.92(0.51)	0	0.75(0.30)	1.0(0.43)	1.25(0.38)
Li ₂ O/Al ₂ O ₃	0.61	0.61	0.61	0.61	0.61	0.61
H.T. (°F.—hr.)	1350- 2/3 2100-1	1400-2 2100-1	1350-2 2/3 2100-1	1350-2 2100-1	1350-2 2/3 2100-1	1350-2 2100-1
M.R. Data* (psi × 10 ⁻³)						
as H.T.	13.7[1.1]	47.5[7.5]	13.7[1.1]	43.3	55.7[1.7]	57.9
+NaNO ₃	46.3[8.0]	**124.2[32.9]	46.3[8.0]	121.4[14.3]	126.1[28.5]	138.2[18.2]
8 hr. -750°F.		**119.1[38.3]				
>	32.6	74.1	32.6	88.1+	70.4+	80.3
+KNO ₃	19.4[1.2]	71.6[5.2]				
16 hr. -750°F.						
>	5.7	24.1				

* All samples hand abraded unless marked with an * to indicate ball mill abrasion.

** Duplicate runs.

> = Change in M.R. (Modulus of Rupture) due to ion exchange.

[] Standard deviation.

() Analyzed

+>'s after comparable heat treatment at 2000-1 are 102.8 and 99.4, respectively.

H.T. Heat treatment.

TABLE 1A

	1	3
as H.T. + NaNO ₃ 1/2 hr. -1000°F.	—	152.4[23.1]
as H.T. + NaNO ₃ 1 hr. -1000°F.	73.2[24.4]	152.8[20.2]
>	59.5	109.5

EXAMPLES 6-10.

Another series of fluorine-containing glass-ceramic rods was prepared to show the increased strength obtained by ion exchanging a fluorine-containing, zinc-containing glass-ceramic article. As seen in Examples 9 and 10, the use of an increasingly large amount of F₂ in the composition results in a decrease in the strength obtained. Hence, in Example 10 it can be seen that the use of 1.24 weight percent

F₂ apparently is too much and abraded modulus of rupture drops down to about 41.4×10^{-3} psi. As previously indicated, the modulus of rupture of the ion exchanged, fluorine-containing glass-ceramic article should be at least 85,000 psi and preferably 90,000 psi. In some applications, as previously indicated, the modulus of rupture after mild abrasion preferably is even higher, namely as high as 100,000 psi or more.

TABLE 2

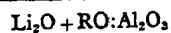
	Analyzed 6	Analyzed 7	Analyzed 8	Analyzed 9	Analyzed 10
SiO ₂	70.2	69.78	70.1	70.1	69.5
Al ₂ O ₃	19.6	19.78	20.0	19.5	19.5
Li ₂ O	3.46	3.52	3.52	3.48	3.56
TiO ₂	1.80	1.80	1.84	1.87	1.89
ZrO ₂	1.49	1.48	1.49	1.54	1.58
Na ₂ O	0.48	0.58	0.50	0.49	0.49
K ₂ O	0.24	0.26	0.18	0.15	0.10
ZnO	1.99	2.57	2.10	2.01	1.92
F ₂	0	0.40	0.44	0.82	1.24
Li ₂ O/Al ₂ O ₃	.60	.60	.61	.61	.62
Li ₂ O+ZnO/Al ₂ O ₃	.73	.72	.77	.74	.74
H.T. (°F. -hr.)	1350-3, 2100-1	1380-2, 2100-1	1350-3, 2000-1	1350-3, 2000-1	1350-3, 2000-1
M.R. Data* (psi $\times 10^{-3}$)					
as H.T.	17.8[1.9]	46.7	38.7[0.9]	64.5[4.8]	66.0[16.4]
+NaNO ₃ 8 hr. -750°F.	36.7[3.0]	86.2[13.3]	92.1[3.9]	73.5[6.2]	41.4[3.5]
>	18.9	39.5	53.4	9.0	-24.6

* All samples hand abraded unless marked with an * to indicate ball mill abrasion.

[] Standard deviation.

H.T. Heat treatment.

EXAMPLES 11—12.



5 Glass-ceramic rods were made from a fluorine-containing, magnesium oxide-containing glass-ceramic article. The results show that increased strength is not obtained by the use of F_2 in the glass-ceramic and the ion exchange thereof when the molar ratio of

is too high (over 0.9:1). The compositions employed and the results obtained are shown in Table 3. 10

TABLE 3

	Analyzed	
	11	12
SiO_2	69.44	69.1
Al_2O_3	19.79	19.8
Li_2O	4.61	4.55
TiO_2	1.83	1.84
ZrO_2	1.47	1.48
Na_2O	0.6	0.59
K_2O	0.31	0.29
MgO	1.99	2.00
F_2	0	0.69
$\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$	0.79	0.78
$\text{Li}_2\text{O} + \text{MgO}$		
Al_2O_3	1.04	0.14
H.T. ($^{\circ}\text{F}$.-hr.)	1300-2, 2000-1	1300-2, 2000-1
M.R. Data* (psi $\times 10^{-3}$)		
as H.T.	20.7[1.5]	32.7
+ NaNO_3 8 hr.-750 $^{\circ}\text{F}$.	70.4[19.1]	56.3
>	49.7	23.6

* All samples hand abraded unless marked with an * to indicate ball mill abrasion.

H.T. Heat treatment.

EXAMPLES 13—17.

5 Fluorine-containing glass-ceramic rods were ion exchanged to show the increased strength obtained by the use of such calcium oxide-containing glass-ceramic articles. The compositions were prepared and glass-ceramic articles made and ion exchanged in a manner similar to that described in Examples 1—5 (see Table 1).

10 As seen in Table 4, the results show the enhancement of the ion exchange process and the great increase in strength obtained by the ion exchange of the fluorine-containing glass-ceramic compositions.

In Table 4, composition 13' was slightly different than composition 13 but was substantially the same. 15

Various finish (heat-treating) temperatures were used on the ion exchanged glass-ceramic articles of the composition shown in Example 16 (Table 4) and composition No. 17 (Table 4). The nucleation of the green glass of Example 16 to a glass-ceramic material was conducted at 1380° C. for 6 hours and the glass of Example 17 at 1350° C. for 4 hours, as indicated in Table 5. As also indicated in Table 5, composition 16 has no F₂ while composition 17 has 0.39 weight percent F₂. 20 25

TABLE 4

	Theoretical				Theoretical	
	13	13'	14	15	16	17
SiO ₂	70.52		69.51	66.62	71.53	70.79
Al ₂ O ₃	19.94		19.94	20.9	20.23	20.02
Li ₂ O	3.51..	(3.32)	3.51	3.8	3.56	3.52(3.55)
TiO ₂	1.8		1.8	1.8	1.4	1.4
ZrO ₂	1.44		1.44	2.0	2.15	2.15
Na ₂ O	0.48	(0.50)	0.48	0.06		(0.10)
K ₂ O		(<0.01)				(<0.01)
CaO	1.32		2.3	3.5	1.10	1.10
Sb ₂ O ₃				0.32		
F ₂	1	(0.44)	1(0.52)	1		1.0(0.39)
Li ₂ O/Al ₂ O ₃	0.6	0.6	0.60	0.62	0.6	0.6
Li ₂ O + CaO						
Al ₂ O ₃	0.71	0.71	0.81	0.92	0.7	0.7
H.T. (°F.-hr.)	1360-3 2100-1	1360-3 2100-1	1375-3 2100-1	1375-3 2100-1	1380-6 2100-1	1350-4 2100-1
M.R. Data* (psi × 10 ⁻³)						
as H.T.	72.9 [10.4]	52.8	67.4	54.0	14.5*	39.4*+
+NaNO ₃ 8 hr.- 750°F.	112.9	119.0[3.0]	108.2[7.3]	81.0[18.3]	39.3*	92.7*
>	50	66.2	40.8*	27.0	24.8	53.3

○ Analyzed

□ Standard deviation

* All samples hand abraded unless marked with an * to indicate ball mill abrasion

+ Value for E2 which is a commercial glass of identical composition to the glass of example 17 except that E2 contains 0.08% less fluorine.

TABLE 5

	16			17		
F_2	0			0.39		
Nucleation ($^{\circ}\text{F}\cdot\text{hr}$)	1380-6			1350-4		
(400 $^{\circ}\text{F}\cdot\text{hr}$. up and down)						
Finish Temp.	Avg. M.R.* ($\text{psi} \times 10^{-3}$)			Avg. M.R.* ($\text{psi} \times 10^{-3}$)		
($^{\circ}\text{F}\cdot\text{hr}$.)	as H.T.	+NaNO ₃ 750 $^{\circ}\text{F}$ -8 hr.	>	as H.T.	+NaNO ₃ 750 $^{\circ}\text{F}$ -8 hr.	> Median M.R. ($\text{psi} \times 10^{-5}$) >
1600-1					6.9[1.5]	
1700-1	12.1[0.9]	5.0[0.4]	-7.1	12.6		
1800-1	11.9[0.8]	7.4[0.7]	-4.5	23.2[1.8]	58.9[8.5]	35.7
1900-1	12.5[0.5]	46.3[0.5]	37.8	26.3	63.2[8.2]	36.9
2000-1	14.8[1.4]	34.2[13.2]	29.4	40.9[5.0]	64.6[28.0]	23.7 75.3 34.4
2100-1	14.5[0.6]	39.3[6.8]	24.8	39.4+	92.7[29.1]	~52 102.3 ~62
2200-1	13.1[2.5]	32.0[12.0]	18.9	60.2[5.4]	91.0[25.6]	30.8 99.5 39

[] Standard deviation

+ see footnotes to Table 4

* All ball mill abraded

It can be seen in Table 5 that generally the finishing step should be conducted at about 1800 $^{\circ}$ to 2200 $^{\circ}$ F. It can be further seen that preferably the temperature of the finishing step should be about 2100 $^{\circ}$ to 2200 $^{\circ}$ F.

EXAMPLE 18.

A fluorine-containing glass-ceramic article was ion exchanged in accordance with the methods described in Example 1. The glass-ceramic article had a modulus of about 50,000 psi after heat treatment. The composition is as follows:—

	Ingredients	Parts by weight
15	SiO ₂	70.15
	Al ₂ O ₃	20.0
	TiO ₂	1.8
	ZrO ₂	1.45
	Sb ₂ O ₃	0.5
20	CaO	1.3
	Li ₂ O	3.5
	Na ₂ O	0.5
	K ₂ O	0.1
25	F ₂	0.6
	Cl ₂	0.1

A sodium for lithium ion exchange using a molten sodium nitrate salt bath increased the abraded modulus of rupture even to over 100,000 psi.

In addition, the article, upon breaking, has a dicing action rather than a shattering action. Thus, the article was outstanding in that it had a very high strength and low thermal expansion in addition to the property of dicing upon breaking.

Other ion exchange medium can be applied to the surface of the glass-ceramic article having the fluorine-containing glass-ceramic composition to provide enhanced ion exchange thereof and the resulting high strength, relatively low expansion glass article. As indicated previously, such glass-ceramic articles have a modulus of rupture of at least 85,000 and preferably even 100,000 psi or more.

In the above examples, the articles or rods that were ball milled were milled in a one-gallon ball mill for 15 minutes using 250 grams of silicon carbide having No. 240 grit size. The hand abraded samples were placed in the chuck of a drill press and a No. 320 abrasive paper held against the sample for about five seconds while the sample was rotating.

In general, the glass-ceramic articles should have a coefficient of thermal expansion of less than $25 \times 10^{-7}/^{\circ}\text{C.}$ and preferably less than $20 \times 10^{-7}/^{\circ}\text{C.}$ ($\Delta T = 0-600^{\circ}\text{C.}$). In the examples, the glass-ceramic starting materials had the following coefficients of thermal expansion ($\Delta T = 0-600^{\circ}\text{C.}$):

Composition	Coefficient of Thermal Expansion ($\times 10^{-7}/^{\circ}\text{C.}$)
7	7
8	7.5
9	15.4
10	21.0
13	9.1
14	14.2
15	17.5

WHAT WE CLAIM IS:—

1. A method of obtaining a glass-ceramic article having a modulus of rupture of over 85,000 psi after mild abrasion, the method comprising the steps of

(1) applying to a surface of the glass-ceramic article containing lithium ions an ion-exchange medium containing alkali metal ions having a larger ionic radius than the lithium ions, the glass-ceramic article comprising in percent by weight

Ingredients	Percent by weight
SiO_2	60—75
Al_2O_3	15—30
Li_2O	3—5.5
F_2	0.2—0.8
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	0—2
$\text{TiO}_2 + \text{ZrO}_2$	2.5—10

wherein TiO_2 and ZrO_2 are present together and the balance, if any, of said article consists of other compatible ingredients and wherein the molar ratio of $\text{R}_2\text{O} + \text{RO}:\text{Al}_2\text{O}_3$ is 0.95 to 0.5:1, where R_2O is the total alkali metal oxide content and RO is the total divalent metal oxide (as hereinbefore defined) content

(2) maintaining on the surface of the glass-ceramic article the ion exchange medium at an elevated temperature sufficiently high and for a period of time sufficient to exchange the lithium ions in the glass-ceramic article with the alkali metal ions of the ion exchange material to provide a compressive stress layer in the article, and

(3) cooling the article to a temperature at which said ion exchange does not occur to provide a glass-ceramic article having a strength of at least 85,000 psi after mild abrasion.

2. A method as claimed in claim 1 wherein the total amount of TiO_2 and ZrO_2 is in the range of 3 to 8% by weight.

3. A method as claimed in claim 1 or 2 in which the total amount of TiO_2 and ZrO_2 is in the range of 3 to 6% by weight.

4. A method as claimed in any one of the preceding claims in which the amount of TiO_2 is 1 to 2% by weight.

5. A method as claimed in any one of the preceding claims in which the amount of TiO_2 is 1.4 to 1.8% by weight.

6. A method as claimed in any one of the preceding claims in which the composition of the glass-ceramic comprises in percent by weight:

Ingredients	Percent by weight
SiO_2	61—71
Al_2O_3	18—28
Li_2O	3.5—4.8
F_2	0.3—0.6

the amount of Na_2O and K_2O being less than 1.5 percent, the amount of TiO_2 and ZrO_2 being in the range of 3.2—5.0%, the molar ratio of $\text{R}_2\text{O} + \text{RO}:\text{Al}_2\text{O}_3$ being 0.9 to 0.6:1.

7. A method as claimed in any one of the preceding claims, in which the composition of the glass-ceramic comprises in percent by weight:

Ingredients	Percent by weight
SiO_2	65—71
Al_2O_3	19—27
Li_2O	4.5—4.8
F_2	0.3—0.55

the amount of Na_2O and K_2O being less than 1.2%, the amount of TiO_2 and ZrO_2 being in the range of 3.2—4.8%, the molar ratio of $\text{R}_2\text{O} + \text{RO}:\text{Al}_2\text{O}_3$ being 0.8:1 to 0.6:1.

8. A method as claimed in claim 1, 2, 3, 4, or 6 in which the composition of the glass-ceramic comprises in percent by weight:

Ingredients	Percent by weight
SiO_2	61.36
Al_2O_3	25.64
Li_2O	4.58
TiO_2	1.83
ZrO_2	2.75
Na_2O	0.55
K_2O	0.55
P_2O_5	1.83
F_2	0.51

9. A method as claimed in any one of claims 1 to 6 in which the composition of the glass-ceramic comprises in percent by weight:

	Ingredients	Percent by weight
5	SiO ₂	63.35
	Al ₂ O ₃	26.6
	Li ₂ O	4.75
	TiO ₂	1.4
	ZrO ₂	2.15
	Na ₂ O	1.0
	F ₂	0.30

10. A method as claimed in any one of claims 1 to 6 in which the composition of the glass-ceramic comprises in percent by weight:

	Ingredients	Percent by weight
15	SiO ₂	62.85
	Al ₂ O ₃	26.6
	Li ₂ O	4.75
	TiO ₂	1.4
	ZrO ₂	2.15
20	Na ₂ O	1.0
	F ₂	0.58

11. A method as claimed in any one of claims 1 to 4, 6 or 7 in which the composition of the glass-ceramic comprises in percent by weight:

	Ingredients	Percent by weight
30	SiO ₂	70.1
	Al ₂ O ₃	20.0
	Li ₂ O	3.52
	TiO ₂	1.84

	Ingredients	Percent by weight
35	ZrO ₂	1.49
	Na ₂ O	0.50
	K ₂ O	0.18
	ZnO	2.10
	F ₂	0.44

12. A method as claimed in any one of claims 1 to 7, in which the composition of the glass-ceramic comprises in percent by weight:

	Ingredients	Percent by weight
45	SiO ₂	70.52
	Al ₂ O ₃	19.95
	Li ₂ O	3.51
	TiO ₂	1.8
	ZrO ₂	1.44
	Na ₂ O	0.48
50	CaO	1.32
	F ₂	0.44

13. A method as claimed in any one of the preceding claims in which the glass-ceramic

article of step (1) is prepared by heating a thermally crystallizable glass composition that is a precursor for the article at a temperature of 1800° to 2200° F. 55

14. A method as claimed in claim 13 in which the temperature of heating the crystallizable glass composition is 2100° to 2200° F. 60

15. A method as claimed in any one of the preceding claims in which the modulus of rupture is at least 90,000 psi. 65

16. A method as claimed in any one of the preceding claims in which the modulus of rupture is at least 95,000 psi. 70

17. A method as claimed in any one of the preceding claims in which the modulus of rupture is at least 100,000 psi. 75

18. A method as claimed in any one of the preceding claims in which said ion-exchange medium is a sodium nitrate or potassium nitrate salt bath. 80

19. A method as claimed in any one of the preceding claims in which said ion-exchange step temperature is in the range of 750° to 1,000° F. 85

20. A method as claimed in any one of the preceding claims in which the duration of said ion-exchange step is in the range of $\frac{1}{2}$ to 8 hours. 90

21. A method of obtaining a glass-ceramic article substantially as hereinbefore described with reference to and as illustrated in any one of the Examples. 95

22. A glass-ceramic article made by the method claimed in any one of the preceding claims. 100

23. A glass-ceramic article as claimed in claim 22 having a modulus of rupture of at least 100,000 psi. 105

24. A strengthened glass-ceramic article as claimed in claim 22, or 23 in which the composition of the glass-ceramic article, prior to ion exchange of the article comprises:

Ingredients	Percent by weight
SiO ₂	63.1
Al ₂ O ₃	26.6
Li ₂ O	4.75
TiO ₂	1.4
ZrO ₂	2.15
Na ₂ O	1.0
F ₂	0.43

25. A glass-ceramic article as claimed in claim 22 substantially as hereinbefore described with reference to and as illustrated in any one of Examples 2 to 10, 13 to 15, 17 or 18. 110

26. A glass ceramic article comprising a composition as defined in any one of claims 1 to 21 in which the surface layer of said glass-ceramic has a compressive stress provided by ion-exchanging lithium ions in the glass-ceramic with alkali metal ions having a larger ionic radius than said lithium ions. 115

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